Transition elements are metals. You will be concerned only with the first row of transition elements, from titanium to copper. They are located in the d-block of the Periodic Table because the outermost electrons are in the d sub-shell.

There are many different things to learn about transition elements. Here is a checklist. Make sure you cover them all:

- definition of a transition element
- electron configurations of the elements and their ions
- oxidation states
- catalytic behaviour
- hydroxides
- complex ions
- ligand substitution
- redox reactions and titration calculations.

**Definition of a transition element**

A transition element has at least one ion with an incomplete d sub-shell.

**Electron configuration of the d-block elements**

<table>
<thead>
<tr>
<th>Element</th>
<th>Symbol</th>
<th>Configuration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Scandium</td>
<td>Sc</td>
<td>[Ar] 3d¹ 4s²</td>
</tr>
<tr>
<td>Titanium</td>
<td>Ti</td>
<td>[Ar] 3d² 4s²</td>
</tr>
<tr>
<td>Vanadium</td>
<td>V</td>
<td>[Ar] 3d³ 4s²</td>
</tr>
<tr>
<td>Chromium</td>
<td>Cr</td>
<td>[Ar] 3d⁵ 4s¹</td>
</tr>
<tr>
<td>Manganese</td>
<td>Mn</td>
<td>[Ar] 3d⁵ 4s²</td>
</tr>
<tr>
<td>Iron</td>
<td>Fe</td>
<td>[Ar] 3d⁶ 4s²</td>
</tr>
<tr>
<td>Cobalt</td>
<td>Co</td>
<td>[Ar] 3d⁷ 4s²</td>
</tr>
<tr>
<td>Nickel</td>
<td>Ni</td>
<td>[Ar] 3d⁸ 4s²</td>
</tr>
<tr>
<td>Copper</td>
<td>Cu</td>
<td>[Ar] 3d¹⁰ 4s¹</td>
</tr>
<tr>
<td>Zinc</td>
<td>Zn</td>
<td>[Ar] 3d¹⁰ 4s²</td>
</tr>
</tbody>
</table>

The 3d sub-shell is filled after the 4s sub-shell, so most of the elements have a full 4s sub-shell, 4s². **But note that chromium and copper have 4s¹ electron configurations, not 4s².** This is to allow either a half-filled or a filled d sub-shell to be made – Cr has 3d⁵ 4s¹ and Cu has 3d¹⁰ 4s¹. A half-filled or completely filled sub-shell is more stable, so it makes sense in energy terms for chromium and copper to have these electron configurations.

**Zinc and scandium** are not included in lists of transition metals although they are in the first row of the d-block. This is because:

- Zinc forms one ion, Zn²⁺, with an electron configuration of 1s² 2s² 2p⁶ 3s² 3p⁶ 3d¹⁰. This means that its only ion has a full, not a partially full, d sub-shell – so zinc is not a transition element.
• Scandium forms one ion, Sc\textsuperscript{3+}, with an electron configuration of 1s\textsuperscript{2} 2s\textsuperscript{2} 2p\textsuperscript{6} 3s\textsuperscript{2} 3p\textsuperscript{6}. This is the main ion, and it has only empty d orbitals, and so scandium is excluded from the list of transition metals.

• We commonly say that scandium and zinc are not transition elements, but they are d-block elements.

Electron configurations of the ions
The transition elements form positive ions, as they are metals. This means that when an ion is formed, electrons are removed from the atom.

You must remember that the 4s electrons are removed first.

■ WORKED EXAMPLE 1
Give the electron configuration of Cu\textsuperscript{2+}.

STEP 1 Write down the electron configuration of the atom, Cu.

\[ \text{[Ar]} \ 3d^{10} \ 4s^1 \]

STEP 2 The ion has a 2+ charge so two electrons are removed. One is taken from the 4s sub-shell, the other from the 3d sub-shell.

So the electron configuration of Cu\textsuperscript{2+} is: 1s\textsuperscript{2} 2s\textsuperscript{2} 2p\textsuperscript{6} 3s\textsuperscript{2} 3p\textsuperscript{6} 3d\textsuperscript{9}.

■ WORKED EXAMPLE 2
Give the electron configuration of Fe\textsuperscript{3+}.

STEP 1 Write down the electron configuration of the atom, Fe.

\[ \text{[Ar]} \ 3d^6 \ 4s^2 \]

STEP 2 The ion has a 3+ charge so three electrons are removed. Two are taken from the 4s sub-shell, the other from the 3d sub-shell.

So the electron configuration of Fe\textsuperscript{3+} is: 1s\textsuperscript{2} 2s\textsuperscript{2} 2p\textsuperscript{6} 3s\textsuperscript{2} 3p\textsuperscript{6} 3d\textsuperscript{5}.

Quick check 3 and 4

Quick check 4

Examiner tip
If a d-block element has a white compound, in that oxidation state it will probably have a completely full or empty d sub-shell. Colour is associated with partly filled d-orbitals.

QUICK CHECK QUESTIONS

1. Explain what is meant by the term transition element.
2. Give the electron configurations of manganese, Mn, and chromium, Cr.
3. Give the electron configurations of Mn\textsuperscript{2+} and Cr\textsuperscript{3+}.
4. Explain why you would not expect compounds of Cu\textsuperscript{+} ions to be coloured whilst those of Cu\textsuperscript{2+} are different colours.
Transition elements – oxidation states, catalytic behaviour and the hydroxides

Oxidation states

One characteristic of the transition elements is that they form compounds and ions with different oxidation states. In forming ions the two electrons in the 4s orbital are lost first. The 3d and 4s energy levels are close in energy and therefore the 3d electrons can also be lost in forming ions.

You have to learn the different oxidation states of iron and copper.

- Iron can have +2, +3, +4, +5 and +6 oxidation states. The +2 and +3 oxidation states are the most common.
- Copper can have +1, +2 and +3 oxidation states. The +1 and +2 oxidation states are the most common.

Catalytic behaviour

Transition metals and their compounds are very good catalysts. There are two reasons for this:

- They can have different oxidation states, so they can gain and lose electrons in moving between these oxidation states, thus facilitating and speeding up redox reactions.
- They provide sites at which reactions can take place, because they bond to a wide range of ions and molecules in solution and as solids.

Examples of industrial catalysts are:

- finely divided Fe or Fe₂O₃ in the production of ammonia
  \[ \text{N}_2(g) + 3\text{H}_2(g) \rightleftharpoons 2\text{NH}_3(g) \]
- solid V₂O₅ in the production of sulfur trioxide, used to make sulfuric acid
  \[ 2\text{SO}_2(g) + \text{O}_2 \rightleftharpoons 2\text{SO}_3(g) \]
- finely divided Ni in the hydrogenation of alkenes
  \[ \text{CH}_2=\text{CH}_2(g) + \text{H}_2 \rightarrow \text{CH}_3\text{CH}_3(g) \]
Transition metal hydroxides

Transition metal ions react with the hydroxide ion in aqueous solution to give a solid.

\[
\text{OH}^- (aq) + \text{transition metal ion(aq)} \rightarrow \text{metal hydroxide(s)}
\]

Example:

The reaction between aqueous copper sulfate and aqueous sodium hydroxide is

\[
\text{CuSO}_4(aq) + 2\text{NaOH}(aq) \rightarrow \text{Cu(OH)}_2(s) + \text{Na}_2\text{SO}_4(aq)
\]

The colour of the metal hydroxide can be used to identify the metal.

You need to know the colours of copper (II) hydroxide, iron(II) and iron(III) hydroxides, and cobalt(II) hydroxide. The list below shows the equations for the reactions and the colours of the aqueous solutions and precipitates obtained.

\[
\begin{align*}
\text{Cu}^{2+} (aq) & \quad \text{blue} + 2\text{OH}^- (aq) \rightarrow \text{Cu(OH)}_2(s) \quad \text{blue} \\
\text{Fe}^{2+} (aq) & \quad \text{pale green} + 2\text{OH}^- (aq) \rightarrow \text{Fe(OH)}_2(s) \quad \text{green} \\
\text{Fe}^{3+} (aq) & \quad \text{yellow/orange} + 3\text{OH}^- (aq) \rightarrow \text{Fe(OH)}_3(s) \quad \text{red-brown/rust} \\
\text{Co}^{2+} (aq) & \quad \text{pink} + 2\text{OH}^- (aq) \rightarrow \text{Co(OH)}_2(s) \quad \text{blue-green and then pink}
\end{align*}
\]

Although these reactions are the only ones you must know, make sure you can predict the reaction between any transition metal ion and aqueous sodium hydroxide.

WORKED EXAMPLE

Predict the formula of the precipitate formed when aqueous sodium hydroxide is added to an aqueous solution of CrCl\(_3\)(aq).

**STEP 1** Work out the formula of the transition metal ion:

In CrCl\(_3\) the chromium ion must be Cr\(^{3+}\).

**STEP 2** The charge on the metal ion is balanced by the number of hydroxide ions in the precipitate:

The charge is 3+ so three OH\(^-\) ions are needed.

**STEP 3** Write the ionic equation:

\[
\text{Cr}^{3+}(aq) + 3\text{OH}^- (aq) \rightarrow \text{Cr(OH)}_3(s)
\]

QUICK CHECK QUESTIONS

1. Explain what is meant by the term *transition element*.
2. Suggest why *finely divided* iron is used as a catalyst in the production of ammonia.
3. **(a)** A transition metal ion in aqueous solution (X) was added to aqueous sodium hydroxide. A brown precipitate appeared. Identify the transition metal ion and write an ionic equation for the reaction.
   **(b) (i)** What is the colour of the aqueous solution of the transition metal ion, X?
   **(ii)** If sulfur dioxide gas is passed through the aqueous solution of X, the solution changes in colour to pale green. What is the ion formed in this reaction?
   **(iii)** What would you see if sodium hydroxide was added to this green solution?
A complex ion is a transition metal atom or ion + ligands. A ligand is a molecule or ion which donates a pair of electrons to the transition metal ion in a complex to form a dative covalent (or coordinate) bond. An example of a complex ion is \([\text{Cu}(\text{H}_2\text{O})_6]^{2+}\). This formula is used to show that Cu\(^{2+}\) is surrounded by six H\(_2\)O molecules. The H\(_2\)O molecules are the ligands. Square brackets go round the whole complex and the total charge of the complex ion goes outside these square brackets. The ligands are shown in normal brackets, with the number of ligands at the end. The number of coordinate bonds round the central ion is called the coordination number.

Shapes of complex ions

Complex ions occur in various shapes. The three most common shapes are shown in the table below:

<table>
<thead>
<tr>
<th>Octahedral</th>
<th>Tetrahedral</th>
<th>Square planar</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coordination number 6</td>
<td>Coordination number 4</td>
<td>Coordination number 4</td>
</tr>
<tr>
<td>Bond angle 90°</td>
<td>Bond angle 109.5°</td>
<td>Bond angle 90°</td>
</tr>
<tr>
<td>e.g. [Cu(H(_2)O)(_6)]^{2+})</td>
<td>e.g. CuCl(_4^{2-})</td>
<td>e.g. [Ni(NH(_3))(_2)Cl(_2)]</td>
</tr>
</tbody>
</table>

Types of ligand

- Ligands can be neutral or anionic (negatively charged).
- Ligands can donate one pair of electrons (monodentate), two pairs of electrons (bidentate) or several pairs of electrons (multidentate).

Here are the most common ligands you will come across.

<table>
<thead>
<tr>
<th>Ligand</th>
<th>Formula</th>
<th>Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>H(_2)O</td>
<td>monodentate</td>
</tr>
<tr>
<td>Ammonia</td>
<td>NH(_3)</td>
<td>monodentate</td>
</tr>
<tr>
<td>Chloride ion</td>
<td>Cl(^-)</td>
<td>monodentate</td>
</tr>
<tr>
<td>Hydroxide ion</td>
<td>OH(^-)</td>
<td>monodentate</td>
</tr>
<tr>
<td>Cyanide ion</td>
<td>CN(^-)</td>
<td>monodentate</td>
</tr>
<tr>
<td>Ethane-1,2-diamine (abbreviated to en)</td>
<td>H(_2)NCH(_2)CH(_2)NH(_2)</td>
<td>bidentate</td>
</tr>
<tr>
<td>EDTA(^{4-})</td>
<td></td>
<td>multidentate (hexadentate)</td>
</tr>
</tbody>
</table>
Stereoisomerism in transition metal complexes

There are two types of stereoisomerism and you will have come across both types when you studied alkenes at A2 level (cis–trans as a special case of E/Z isomerism) and stereoisomerism (optical isomerism) at A2.

Cis–trans isomerism

Cis–trans isomerism in transition metals is different from that found in the alkenes because there is no double bond present, just the arrangement of ligands around a central transition metal ion. The cis isomer has two identical groups lying on one side of the metal ion (with a bond angle of 90° between them), whilst the trans isomer has two identical groups lying on opposite sides of the ion (180° apart).

The two examples below illustrate how cis–trans isomerism can occur for square planar and octahedral complexes.

Optical isomerism

In optical isomerism there are two isomers that are non-superimposable mirror images of each other. An example of this is the [Ni(H₂NCH₂CH₂NH₂)₃]²⁺ complex.

The H₂NCH₂CH₂NH₂ ligand is a bidentate ligand and can be represented as shown opposite when drawing complexes.

The two isomers of [Ni(H₂NCH₂CH₂NH₂)₃]²⁺ are shown below.

Quick check 4

Quick check 5

QUICK CHECK QUESTIONS

1 Using [Cu(H₂O)₆]²⁺ as an example, explain the terms ligand, complex, octahedral and coordination number.
2 Draw the following complexes:
   (a) [Fe(H₂O)₆]²⁺
   (b) CoCl₄²⁻.
3 Using H₂NCH₂CH₂NH₂ as an example, explain the term bidentate ligand.
4 Draw the two isomers of [Pt(NH₃)₂Cl₂].
5 Draw the two optical isomers of [CoCl₄(H₂NCH₂CH₂NH₂)₂].
Some ligands combine more strongly with transition metal ions than others. A ligand that binds strongly can displace a ligand that binds more weakly. This is called **ligand substitution**. You can see ligand substitution in experiments because different ligands change the colour of the solution as a different complex is formed.

There are certain ligand substitution reactions you must know, along with the colour changes accompanying them. These are illustrated below. The diagrams show the structures of the complexes and the colour changes occurring.

**Example 1** Ammonia solution is added to a solution of aqueous copper(II) ions (e.g. aqueous copper(II) sulfate solution):

\[
[Cu(NH_3)_4(H_2O)_2]^{2-} (aq) \rightarrow 4H_2O(l) \quad \text{blue} \rightarrow [Cu(H_2O)_6]^{2+} (aq) \rightarrow 4NH_3(aq) \quad \text{deep blue}
\]

**Example 2** Concentrated hydrochloric acid (Cl\(^-\)) is added to aqueous copper(II) ions:

\[
[Cu(H_2O)_6]^{2+} (aq) + 4Cl^- (aq) \rightarrow CuCl_4^{2-} (aq) + 4H_2O(l) \quad \text{Green due to a mixture of the two complexes} \rightarrow \text{CuCl}_4^{2-} (aq) + 4H_2O(l) \quad \text{yellow}
\]

**Example 3** Water is added to a solution of CoCl\(_4^{2-}\) ions:

\[
\text{CoCl}_4^{2-} (aq) + 6H_2O(l) \rightarrow \text{[Co(H}_2O)_6]^{2+} (aq) + 4Cl^- (aq) \quad \text{blue} \rightarrow \text{[Co(H}_2O)_6]^{2+} (aq) + 4Cl^- (aq) \quad \text{pink}
\]

---

**Module 3**

**Examiner tip**
Both these complexes have six ligands, so they are octahedral in shape.

**Quick check 1**

**Quick check 2**

**Examiner tip**
To get the overall charge on the complex CoCl\(_4^{2-}\) ion you add together the charge on the metal ion and the charges on the ligands. Overall charge = charge on metal ion + charges on ligands.

**Examiner tip**
This is used as a test for water. The CoCl\(_4^{2-}\) ion is on cobalt chloride paper. When water is added it turns from blue to pink.
Haemoglobin

In haemoglobin a central Fe" ion is the ion in an octahedral complex comprising four dative covalent bonds from the nitrogens in a porphyrin ring, and one from a nitrogen on one of the amino acids on the globin molecule, which is the protein part of the haemoglobin molecule. The sixth ligand in the complex is oxygen.

Carbon monoxide is toxic because it binds to the central Fe" ion more strongly than oxygen and replaces it in the complex. This means that oxygen cannot be carried around the body, causing asphyxiation.

The reaction is HbO2(aq) + CO(g) ⇌ HbCO(aq) + O2(g)

Stability constants and ligand substitution

When a ligand is added to a solution of the complex formed between water and a transition metal ion, an equilibrium is established as ligand substitution takes place. You have to be able to write the equilibrium constant for this equilibrium, called the stability constant.

WORKED EXAMPLE

How do we write the stability constant when Cl⁻ substitutes for water molecules?

STEP 1 Write the equation for the reaction. This always concerns the complex containing water as a reactant:

\[ [\text{Cu(H}_2\text{O)}_6]^{2+} + 4\text{Cl}^-(aq) \rightleftharpoons \text{CuCl}_4^{2-} (aq) + 6\text{H}_2\text{O(l)} \]

STEP 2 Write the equilibrium constant for the reaction.

\[ K_c = \frac{[\text{CuCl}_4^{2-}] \cdot [\text{H}_2\text{O}]^6}{[[\text{Cu(H}_2\text{O)}_6]^{2+}] \cdot [\text{Cl}^-]^4} \]

STEP 3 Simplify this by omitting the concentration of water as a factor. This is because the concentration is a constant. The new equilibrium constant is the stability constant.

\[ K_{\text{stab}} = \frac{[\text{CuCl}_4^{2-}]}{[[\text{Cu(H}_2\text{O)}_6]^{2+}] \cdot [\text{Cl}^-]^4} \]

STEP 4 Add the units to your expression. In this case we have:

\[ \text{units} = \frac{\text{mol dm}^{-3}}{\text{mol dm}^{-3} \times (\text{mol dm}^{-3})^4} = \frac{1}{(\text{mol dm}^{-3})^4} = \text{dm}^{12} \text{ mol}^{-4} \]

The magnitude of the stability constant is a measure of how strongly the ligand binds to the central metal ion. The greater \( K_{\text{stab}} \) the stronger the binding.

The strength of binding of some ligands to Cu" follows the following trend:

EDTA" > NH₃ > Cl⁻ > H₂O

QUICK CHECK QUESTIONS

1. Using the reaction

\[ [\text{Cu(H}_2\text{O)}_6]^{2+} (aq) + 4\text{NH}_3(aq) \rightleftharpoons [\text{Cu(NH}_3)_4(H}_2\text{O)}_2]^{2+} (aq) + 4\text{H}_2\text{O(l)} \]

(a) Explain the term ‘ligand substitution’.

(b) Write the expression for the stability constant.

2. Give the colour changes occurring when Cl⁻ ions are added to a solution of [Cu(H₂O)₆]²⁺ ions.

3. Explain why carbon monoxide poisoning is caused by ligand substitution.
You have met redox reactions before in the AS course (AS Revision Guide page 16) and on page 72 of this book. Now you will study some redox reactions involving transition metal ions. There are many of these, because transition elements have several different oxidation states.

Often half-equations and ionic equations are used to show redox behaviour.

**Redox behaviour in iron**

\[
\text{Fe}^{3+}(aq) + e^- \rightleftharpoons \text{Fe}^{2+}(aq)
\]

Iron can change from:
- oxidation state +2 to +3 (oxidation) if an oxidising agent is added to it.
- oxidation state +3 to +2 (reduction) if a reducing agent is added to it.

- \(\text{Fe}^{3+}\) is itself an oxidising agent, because it can oxidise other species by gaining an electron.
- \(\text{Fe}^{2+}\) is itself a reducing agent, because it can reduce other species by donating an electron.

**Example:**

\[
\text{Fe}^{3+}(aq) + 2\text{I}^-(aq) \rightarrow \text{Fe}^{2+}(aq) + \text{I}_2(aq)
\]

You can tell by the colour change that this reaction has happened. \(\text{Fe}^{3+}\) is yellow-orange, \(\text{Fe}^{2+}\) is pale green and \(\text{I}_2\) is brown. The brown colour of the \(\text{I}_2\) masks the pale green of \(\text{Fe}^{2+}\), so the colour change is pale orange to brown.

**Redox behaviour in manganese**

\[
\text{MnO}_4^- + 8\text{H}^+(aq) + 5e^- \rightarrow \text{Mn}^{2+}(aq) + 4\text{H}_2\text{O}(l)
\]

This reaction takes place in acid solution, as you can see by the presence of \(\text{H}^+(aq)\) ions in the equation.

Manganese is reduced in this reaction, so the \(\text{manganate(VII)}\) ion is an oxidising agent.

**Example:**

\[
\text{MnO}_4^- + 5\text{Fe}^{2+} + 8\text{H}^+ \rightarrow \text{Mn}^{2+} + 5\text{Fe}^{3+} + 4\text{H}_2\text{O}
\]

The colour change here is from purple \(\left(\text{MnO}_4^-\right)\) to yellow \(\left(\text{Fe}^{3+}\right)\) – the very pale pink of the \(\text{Mn}^{2+}\) does not show.

**Redox behaviour in chromium**

\[
\text{Cr}_2\text{O}_7^{2-}(aq) + 14\text{H}^+(aq) + 6e^- \rightarrow 2\text{Cr}^{3+} + 7\text{H}_2\text{O}
\]

This reaction is frequently used in organic chemistry, where the orange → green colour change tells you the organic substance has been oxidised (see page 9 and AS Revision Guide page 62).
Titration calculations

You must revise titration calculations because they will be tested!

**KMnO₄ titrations**

Make sure you are familiar with the redox titration between MnO₄⁻ and Fe²⁺ in aqueous acid solution.

- The equation for this reaction is:
  \[ \text{MnO}_4^- (aq) + 5 \text{Fe}^{2+} (aq) + 8 \text{H}^+ (aq) \rightarrow \text{Mn}^{2+} (aq) + 5 \text{Fe}^{3+} (aq) + 4 \text{H}_2\text{O}(l) \]

- The purple aqueous MnO₄⁻ is added from the burette to the aqueous Fe²⁺. It immediately goes colourless as it reacts with the Fe²⁺ (the very pale pink of Mn²⁺(aq) and the pale yellow of dilute Fe³⁺(aq) do not show at these low concentrations).

- The end point is when all the Fe²⁺ has reacted and a permanent pink colour can be seen.

- Remember the acid! It takes part in the reaction, so without acid the reaction will not happen.

**Thiosulfate titrations**

Sodium thiosulfate (containing the S₂O₃²⁻ ion) is a useful reagent because it can be titrated against iodine. It is particularly useful in linked reactions. For example, it can be used to estimate the concentration of Cu²⁺ ions in a solution.

Firstly, excess iodide ions are added to the solution of copper(II) ions:

\[ 2\text{Cu}^{2+} (aq) + 4\text{I}^- (aq) \rightarrow 2\text{CuI} + \text{I}_2 \]

The iodine liberated is then titrated against standard sodium thiosulfate solution:

\[ \text{I}_2 + 2\text{S}_2\text{O}_3^{2-} \rightarrow \text{S}_4\text{O}_6^{2-} + 2\text{I}^- \]

From these two equations it can be seen that:

\[ 2\text{Cu}^{2+} \equiv \text{I}_2 \equiv 2\text{S}_2\text{O}_3^{2-} \]

Therefore the number of thiosulfate ions = the number of copper(II) ions.

We can then use our equations for moles in solution to find the concentration of the copper.

**Quick check questions**

1. Hydrogen peroxide, H₂O₂, is an oxidising agent. Construct the equation for the reaction between hydrogen peroxide and Fe²⁺ ions in aqueous solution.

2. A student weighed out 5.56 g of FeSO₄·7H₂O, dissolved it in dilute sulfuric acid and made up the solution to 250 cm³ in a volumetric flask using distilled water. She then titrated 25 cm³ samples of this solution against potassium manganate(VII) solution. The iron(II) sulfate solution required 20.0 cm³ for complete reaction.

   - Calculate the concentration of the Fe²⁺ ion in the iron(II) sulfate solution.
   - Calculate the concentration of the potassium manganate solution.

3. Brass is an alloy of copper and zinc. To find the percentage of copper in a sample of brass, a student dissolved 2.20 g of the brass in concentrated nitric acid and made the resulting solution up to 250 cm³ in a volumetric flask. He then took 25.0 cm³ samples of this solution, added excess potassium iodide solution and then titrated the iodine liberated against a standard, 0.100 mol dm⁻³ solution of sodium thiosulfate. Starch was used as the indicator. The solution required 22.5 cm³ of sodium thiosulfate for complete reaction.

   - Give the equations for the reaction of Cu²⁺ ions with I⁻ ions and the reaction of iodine with thiosulfate ions.
   - Calculate the concentration of copper ions in the solution and the percentage composition of the sample of brass. (NOTE: zinc does not react with I⁻ ions.)
1. Copper readily forms complexes with water, ammonia and chloride ions, and pairs of these ions can coexist in different equilibria.
   (a) Concentrated hydrochloric acid is added to a solution containing 
   \[ \text{[Cu(H}_2\text{O)}_6]\text{^2+}(aq) \] until there is a high concentration of Cl\(^-\).
   \[ \text{[Cu(H}_2\text{O)}_6]\text{^2+}(aq) + 4\text{Cl}^- (aq) ⇌ \text{[CuCl}_4]\text{^2-}(aq) + 6\text{H}_2\text{O(l)} \]
   pale blue yellow
   (i) Using one or both of the two complexes given above, explain what is meant by the following terms:
   I coordinate bonding [2]
   II ligand [2]
   III complex [2]
   (ii) Draw the two complexes described in the equilibrium. [4]

(b) (i) State le Chatelier’s principle. [2]
   (ii) For the equilibrium shown, use le Chatelier’s principle to deduce what is observed as the acid is added. [3]

(c) The equilibrium constant, \( K_c \), for the equilibrium in (a) may be written as:
   \[ K_c = \frac{[\text{[CuCl}_4]\text{^2-}][\text{H}_2\text{O}]}{[\text{[Cu(H}_2\text{O)}_6]\text{^2+}][\text{Cl}^-]^4} \]
   It is possible in aqueous solution to simplify this expression to:
   \[ K'_c = \frac{[\text{[CuCl}_4]\text{^2-}]}{[\text{[Cu(H}_2\text{O)}_6]\text{^2+}][\text{Cl}^-]^4} \]
   The numerical value of \( K'_c \), for this equilibrium, at 25 °C, is 4.17 × 10^5.
   (i) What are the units of \( K'_c \)? [1]
   (ii) An equilibrium mixture, at 25 °C, contained 1.17 × 10^-5 mol dm\(^{-3}\) \[\text{[Cu(H}_2\text{O)}_6]\text{^2+}(aq)\] and 0.800 mol dm\(^{-3}\) Cl\(^-\). Calculate the equilibrium concentration of \[\text{[CuCl}_4]\text{^2-}(aq)\]. [2]
   (iii) Suggest why, in aqueous solution, it is possible to simplify \( K_c \) to \( K'_c \). [2]
   [TOTAL 20 marks]

2. (a) (i) With the aid of examples, explain the meaning of the terms strong acid and weak acid. [2]
   (ii) Using the ethanoic acid/sodium ethanoate mixture as an example, explain how a buffer solution works. [5]

(b) Assuming the temperature to be 25 °C, what is the pH of:
   (i) 0.05 mol dm\(^{-3}\) hydrochloric acid [1]
   (ii) 0.01 mol dm\(^{-3}\) sodium hydroxide? [2]

(c) Benzoic acid, \( C_6H_5COOH \), is a weak acid with an acid dissociation constant, \( K_a \), of 6.3 × 10^-5 mol dm\(^{-3}\) at 25 °C.
   (i) Calculate the pH of 0.020 mol dm\(^{-3}\) benzoic acid at this temperature. [3]
   (ii) Draw a sketch graph of the change in pH which occurs when 0.020 mol dm\(^{-3}\) potassium hydroxide is added to 25 cm\(^3\) of 0.020 mol dm\(^{-3}\) benzoic acid until in excess. [3]
   (iii) The \( pK_a \) values of some indicators are:
   - thymol blue 1.7
   - congo red 4.0
   - thymolphthalein 9.7
   Which of these indicators would be most suitable for determining the end point of the titration between the benzoic acid and potassium hydroxide in (ii)? Explain your answer [2]
   [TOTAL 18 marks]
Methanol, CH₃OH, is used as an alternative fuel to petrol in racing cars. Although methanol is less volatile than petrol, its combustion in these engines is more complete.

(a) Enthalpy changes can be determined indirectly using standard enthalpy changes of formation.

(i) Write the balanced equation for the combustion of methanol.

(ii) Calculate the standard enthalpy change of combustion of methanol using the following data.

<table>
<thead>
<tr>
<th>Compound</th>
<th>ΔH/kJ mol⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₃OH(l)</td>
<td>-239</td>
</tr>
<tr>
<td>CO₂(g)</td>
<td>-394</td>
</tr>
<tr>
<td>H₂O(l)</td>
<td>-286</td>
</tr>
</tbody>
</table>

(iii) The molar entropies of the reactants and products involved in the reaction are given below:

<table>
<thead>
<tr>
<th>Compound</th>
<th>ΔS J K mol⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₃OH(l)</td>
<td>127</td>
</tr>
<tr>
<td>CO₂(g)</td>
<td>214</td>
</tr>
<tr>
<td>H₂O(l)</td>
<td>70</td>
</tr>
<tr>
<td>O₂(g)</td>
<td>127</td>
</tr>
</tbody>
</table>

Using these values calculate the standard entropy change for the reaction.

(b) Calculate the molar free energy change for the reaction at 298 K and hence explain whether or not it is a spontaneous reaction at this temperature.

(c) At 298 K the combustion of methanol requires, for example, a lighted spill or a spark from an ignition coil. In the light of your answer to part (c), explain this fact.

(d) One of the consequences of the heat generated by a car engine is the formation of nitrogen oxide, NO.

When the nitrogen monoxide leaves the car engine it is oxidised to a gas in which the oxidation number of the nitrogen is +4.

(i) Identify the product and write the balanced symbol equation for the reaction.

(ii) Explain why it is a redox reaction.

In an experiment to investigate the effects of changing concentrations on the rate of reaction, the following results were obtained.

<table>
<thead>
<tr>
<th>Experiment number</th>
<th>Initial concentration O₂/10⁻² mol dm⁻³</th>
<th>Initial concentration NO/10⁻² mol dm⁻³</th>
<th>Initial rate of disappearance of NO/10⁻⁴ mol dm⁻³s⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.0</td>
<td>1.0</td>
<td>0.7</td>
</tr>
<tr>
<td>2</td>
<td>1.0</td>
<td>2.0</td>
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</tr>
<tr>
<td>3</td>
<td>1.0</td>
<td>3.0</td>
<td>6.3</td>
</tr>
<tr>
<td>4</td>
<td>2.0</td>
<td>2.0</td>
<td>5.6</td>
</tr>
<tr>
<td>5</td>
<td>3.0</td>
<td>3.0</td>
<td>18.9</td>
</tr>
</tbody>
</table>